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16. ABSTRACT

The paper gives an overview of research activities in EPA's Air and Energy Engineering Research Laboratory, including the identification, assessment, and control of sources of volatile organic compounds (VOCs), hazardous air pollutants (HAPs), and chlorofluorocarbons (CFCs). VOCs, HAPs, and CFCs cause serious detrimental environmental effects, including human health effects, materials damage, and crop/forest losses resulting from (1) tropospheric (or boundary layer) ozone concentrations which are too high, (2) increased ultraviolet radiation reaching the surface of the Earth due to ozone depletion in the stratosphere, and (3) exposures of human lung tissue (and other organs) to HAPs. EPA's Office of Air and Radiation has established a national ambient air quality standard (NAAQS) of 0.12 ppm for ozone. This standard is routinely exceeded in more than 60 areas nationwide. This, coupled with the fact that some areas may not be able to attain the NAAQS for the next 20-30 years, causes serious concerns for human health and welfare. These concerns are heightened by the fact that some scientists are calling for an even more stringent ozone NAAQS. Health impacts from exposure to HAPs include neurological, behavioral, reproductive, and carcinogenic effects. A major concern is that some of these compounds may cause cancer.

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CONFERENCE ON ENVIRONMENTAL CONTROL '89

CLEMSON UNIVERSITY
COLLEGE OF ENGINEERING
CONTINUING ENGINEERING EDUCATION

AIR TOXICS DEVELOPMENTS AT EPA

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INTRODUCTION

Volatile organic compounds (VOC's), chlorofluorocarbons (CFC's), and hazardous air pollutants (HAP's) are known to cause serious detrimental environmental effects. The effects include human health effects, materials damage, and crop/forest losses resulting from: (1) tropospheric or "boundary layer" ozone concentrations which are too high; (2) increased ultraviolet radiation reaching the surface of the Earth due to ozone depletion in the stratosphere, and (3) exposures of human lung tissue (and other organs) to hazardous air pollutants.

U. S. EPA's Office of Air and Radiation has established a national ambient air quality standard (NAAQS) of 0.12 ppm for ozone. This standard is routinely exceeded in more than 60 areas nationwide.(1)(2) This, coupled with the fact that some areas may not be able to attain the standard for the next 20-30 years, causes serious concerns for human health and welfare. These concerns are heightened by the fact that some scientists are calling for an even more stringent ozone standard than the current 0.12 ppm standard.

Life on Earth has evolved under the protective shield of the stratospheric ozone layer. Now, anthropogenic activities have been implicated in the partial removal of the protective shield. CFC's last a long time (100's of years) in the environment, and they participate in chemical reactions which deplete stratospheric ozone. It is uncertain what the results of such fundamental changes in our environment will be over the long term.

HAP's are those air pollutants which fall in the category established by these boundaries: (1) they are for the most part produced by the activities of humans, (2) they are measurable in air, and (3) they are not among the "criteria pollutants" as currently defined by EPA. Obviously, 1000's of pollutants fit these criteria. The health impacts from exposure to HAP's include neurological, behavioral, reproductive, and carcinogenic effects.(3) A major concern is the possibility that some of these compounds may cause cancer.(4)

Engineers and scientists in EPA's Office of Research and Development have undertaken the task of identifying, assessing, and controlling the sources of VOC's, HAP's, and CFC's. This paper provides an overview of these research activities in EPA's Air and Energy Engineering Research Laboratory at Research Triangle Park, North Carolina.

OZONE NON-ATTAINMENT RESEARCH PROGRAM

The research programs to improve compliance with the NAAQS for ozone include VOC and HAP source assessment, emissions minimization, and control technology assessment. Successful implementation of the programs will contribute to: (1) more extensive attainment of the current NAAQS for ozone and (2) reduction in adverse health effects resulting from exposures to HAP's. Initially, the

VOC/HAP research program focused on large point sources, such as reactors, furnaces, and boilers, which emit more than 100 tons of VOC/year. The research program has provided source and control technology assessments which have been used in the development of regulations. In addition, the research program has supported Agency goals by enhancing existing control technologies and developing innovative technologies which may permit control of previously uncontrolled emissions.

In recent years, the research program has also been concerned with the large variety of small sources found in urban areas. Some sources have been identified and emissions have been quantified. Mitigation scenarios which include prevention (e.g., alternative chemicals, feedstock and product substitution, recycle and reuse) and innovative control approaches are being developed. Significant components of this work are: (1) systems management to better understand the nature of sources and the preventability of emissions, (2) product management to minimize emissions, (3) process management to minimize emissions, and (4) a program of rapid engineering response to state and local agencies.

Major unresolved scientific issues in the research program are: (1) the need for more extensive, comprehensive, and accurate characterization of area sources, (2) development and testing of integrated mitigation scenarios involving combinations of prevention and control approaches, (3) identification and circumvention of technical barriers to the effective use of available and emerging control techniques, (4) assessment of prevention and control approaches in attainment and in non-attainment areas to determine the factors which comprise the greatest impediments to successful emissions reduction, (5) definition of means for increasing field reliability of existing controls, and (6) development of a quality assurance system for improving permitting decisions. Specific projects currently underway or planned include:

- Ranking of VOC sources considering seasonal and regional emissions
- Ranking of solvents by importance to state/local officials
- Background problem definition; identification of opportunities for the engineering program to contribute to solutions
- Identification of area and small point VOC sources for which controls are not currently available
- Identification of VOC control options for non-mobile source fuel use; e.g., lawn mowers, portable generators
- Determination of types and quantities of VOC's used as "inerts" in pesticides; preliminary evaluations of options for elimination or reduction of the "top 20" VOC's in terms of quantities used
- Determination of the types and quantities of VOC's used in aerosol products in the U.S.; evaluation of existing alternative

products and packaging

- In-house laboratory assessment of the types and quantities of VOC's released by specific aerosol products

STRATOSPHERIC OZONE RESEARCH PROGRAM

On January 1, 1989, the Montreal Protocol entered into force, committing nations responsible for at least two-thirds of the world's production of chlorofluorocarbons (CFC's) to cooperative continuation of significant steps to reduce the production and consumption of CFC's and halons which contribute to depletion of stratospheric ozone. A recent EPA projection of potential stratospheric ozone depletion indicates that, even with 100 percent global participation in the Protocol, the chlorine concentration in the atmosphere will triple by the year 2075.(5) Moreover, according to this EPA analysis, just to stabilize chlorine concentrations at current levels requires an immediate, worldwide, 85 to 100 percent reduction in the use of all fully halogenated compounds and an immediate freeze in methyl chloroform consumption.(5) Stabilizing bromine levels requires a 100 percent reduction of Halon-1301 usage and a 90 to 100 percent reduction of Halon-1211 consumption, with total global participation.(5)

The U.S. EPA has instituted major programs in both the Office of Air and Radiation (OAR) and the Office of Research and Development (ORD) which address the issue of stratospheric ozone depletion. ORD's program will focus on: (1) the effects of increased UV-B radiation on terrestrial ecosystems, aquatic ecosystems, human health, and tropospheric air quality and (2) engineering evaluation and development of control techniques and technologies. The ORD program is structured to answer the following questions:

- How extensive are the potential effects of UV-B radiation? What populations, systems, or substances are at greatest risk?
- How intensive are the effects of UV-B irradiance? What doses would pose a significant risk?
- If the dose of UV-B radiation is reduced, what is the anticipated rate and extent of recovery of sensitive systems?
- What interactions occur between increased UV-B radiation, global climate change, and atmospheric pollutants?
- What mitigation options can be applied? To which systems?

The Air and Energy Engineering Research Laboratory (AEERL) of EPA is engaged in a number of projects related to the protection of stratospheric ozone. One such project is to describe alternatives to CFC propellants in aerosol products. This is an area in which the U.S. clearly can assume world leadership since U.S. aerosol manufacturers have at least 10 years of experience using non-CFC propellants.

The Laboratory also has initiated a modest research program to investigate other chemical alternatives to the Protocol compounds beyond the new HFC-134a, HCFC-123, and HCFC-141b compounds that the chemical industry is pursuing. This research is being conducted by two research teams--one at Clemson University headed by Professor Darryl DesMarteau and one at the University of Tennessee headed by Professor James Adcock. The research involves the synthesis of new fluorinated compounds and the determination of their physical and chemical properties. Promising new compounds produced in the initial phase of this project will be subjected to preliminary screening tests for atmospheric reactivity, acute toxicity, and end-use applicability.

AEERL is also sponsoring a project at the Massachusetts Institute of Technology in cooperation with the Department of Energy's (DOE's) Oak Ridge National Laboratory to investigate ways of maintaining or improving the thermal performance of insulation foams made without the use of CFC's. This is one of several projects suggested by private industry at an insulation foam workshop sponsored by DOE in June 1988.

AEERL has recently undertaken the development of a sampling and analytical protocol to detect the presence of "Protocol compounds" in cellular plastic foams such as flexible polyurethane foam and rigid polyisocyanurate, polystyrene, polyethylene, and phenolic foams. This project will provide a means of identifying and preventing the importation of products containing "Protocol compounds" from nations not party to the Protocol.

WOODSTOVE RESEARCH PROGRAM

Data gathered to date in the "Northeast study" and in other studies showed that stoves using catalytic technology to reduce emissions achieved a 25 percent reduction in emissions in field applications compared to 90 percent or more in laboratory certification tests.(6) Investigations during FY88 focused on determining the reasons for the poor performance of stoves in field use. The FY89 research program will continue the assessment of existing stove designs to obtain the data necessary to identify these reasons and to establish the performance capabilities of current EPA 1990 certified stove technology. Research attention will be focused on assessment of a number of variables, including:

- The way the stoves are operated
- The frequency of fuel loadings
- The impact of fuel loadings on catalytic activity
- The effect of design differences on performance
- Tests of field-aged catalysts to determine the extent to which their catalytic potential has been reduced relative to new catalysts

Stoves selected for the FY89 field study will be subjected to "torture tests" in the laboratory to identify any design weaknesses. Three catalytic and two low-emission, non-catalytic stoves will be used in the laboratory tests.

In addition to the laboratory study, a field test involving homeowners in New York State will be conducted. Homeowner volunteers, selected by the State, will have their current stoves removed and the new technology stoves installed. Flue systems will be upgraded as necessary and the users provided instruction on optimum performance operation of their new stoves. Detailed emissions and operating data will be recorded for 3 months in each home. The gathered data will be reduced and analyzed, and a final report written. Hybrid designs (best stove/best catalyst combinations) and other features to enhance performance will be evaluated.

Work has begun on installation of an in-house woodstove catalyst characterization laboratory. This laboratory at EPA/AEERL will provide the capability to assess and compare used and new catalysts to determine the operating conditions that result in effective operation and long catalyst life. One goal of this laboratory is to define the best hybrid stove design, combining the best non-catalyst stove(s) with the best catalyst(s) to produce a stove that can consistently meet the 1990 New Source Performance Standard (NSPS) for woodstoves in field applications.

CARBON ADSORPTION RESEARCH PROGRAM

Research will be continued in the use of carbon adsorption for the control of VOC and HAP emissions from industrial and commercial operations. In FY 89, research will focus on quantification of the effect of humidity on adsorption capacity for single components. The effects of absolute and relative humidity will be compared in order to determine which variable is best to use for predicting the effect of humidity on adsorption efficiency.

Organics from three different groups have been selected for this study. These organics have been selected because they are commonly found in contaminated air streams and because their physical properties make them suitable for removal by carbon adsorption. The three organics and their respective families are:

- Toluene, aromatic
- Ethanol, alcohol
- Methyl ethyl ketone (MEK), ketone

Data have been collected for toluene and ethanol. Since the data indicate that relative humidity, even below 50 percent, decreases the loading capacity of activated carbon, additional data will be taken at zero moisture and at low moisture content to quantify this effect. The data have also shown an apparent effect of temperature variations on loading capacity at constant

relative humidity.

Initial breakthrough data for ethanol do not look as good as the toluene data. This is probably because ethanol is a polar compound and is weakly adsorbed by activated carbon. Additional data are necessary to confirm these findings and to evaluate mechanisms to explain the apparent differences in adsorptive capacity.

Additional work that is important to incorporate in the program includes:

- Determination of the effect of compound interactions in multi-component adsorption under varying degrees of humidification
- Development of mathematical models which may predict a sorbent's working capacity for the removal of single, specific organic compounds. (Models will take into account a wide range of humidities and will provide the flexibility of incorporating multicomponent interactions.)
- Publication of results to date in peer-reviewed journals

CORONA DESTRUCTION RESEARCH PROGRAM

Corona destruction is an innovative technology which utilizes the application of electrical current across a bed packed with a dielectric material (such as barium titanate). An electrical corona is generated on the surface of the packing, and the corona energy is used for the destruction of VOC's, HAP's, and CFC's in effluent streams.

Initial tests of a corona destruction reactor for the control of toluene emissions were very encouraging. The tests, conducted without benefit of temperature or humidity control, achieved more than 90 percent destruction of the incoming hydrocarbon with little if any formation of other hydrocarbon compounds.

Research will be continued to prove the concept of using corona destruction for controlling VOC's and HAP's from small point sources. One aspect of the research will be to attempt to determine the mechanisms by which destruction of VOC's, CFC's, and other toxics takes place in the corona destruction reactor.

Experiments will be conducted to evaluate the effects of electron acceleration and energy levels on formation of ions and free radicals, and on molecular bond cleavage. Currently, we are investigating the destruction of para-methoxyphenol, a major component of wood combustion emissions. The destruction of other VOC's and HAP's will be also be investigated.

The research will also include an evaluation of the concept of the use of corona destruction combined with integral chemical bonding of halides and other molecular fragments in a fixed-bed, electrified reactor so that the

technology might be used to control CFC emissions. Corona conditions will be induced in beds of high resistivity alkaline material such as lime, and the ability of the reagent to capture halides and other products of the cleavage of molecular bonds will be determined.

PARTICLE CONTROL RESEARCH PROGRAM

Particulate matter is one of the original six "criteria" pollutants. The primary and secondary environmental effects of particle emissions are well-documented and accepted throughout the scientific community. National Ambient Air Quality Standards (NAAQS) and New Source Performance Standards (NSPS) have been established for particles based on these scientific findings.

The standards must be reconsidered and revised based on additional scientific data accumulated since the standards were first promulgated. New data suggest that smaller particles potentially constitute a greater threat to public health and welfare than was known when earlier standards were set. The control of these smaller particles presents significant, new engineering challenges which must be overcome if control adequate to comply with standards is to be achieved.

Recent concerns about inhalable particles in the 10 um size range (PM 10) have increased the need for additional particle control research to enhance the efficiency of currently available control technologies and to develop and prove advanced technologies. The problem is further complicated by the fact that atmospheric particulate loadings include primary particles (those emitted directly) and secondary particles (those formed in the atmosphere from primary emissions). Particulate loadings include the expected inorganic "ash," but they also include primary and secondary air toxics particles. Some of these particles are formed from condensable components which are ineffectively controlled by existing, conventional control technologies. As many as 22 areas nationwide are unable to comply with existing NAAQS for particles.(7)

Current activities include problem definition, priority setting, and the provision of input for regulatory decision making. Future research program activities will respond to the fact that current needs to achieve regulatory goals have outstripped the capability of conventional control technologies to: (1) achieve greater efficiencies; (2) effectively collect the smaller fractions of particulate emissions; and (3) control toxic pollutants which escape conventional collection almost completely and then contribute to particulate loadings by condensation in the atmosphere.

This research program will allow the enhancement of conventional technologies; the modelling of these technologies to encourage wider and wiser use; the addition of innovative enhancements to conventional technologies, making them more efficient and giving them wider applicability; and finally, the conception, development, and testing of advanced technologies which may contribute to the achievement of environmental goals.

MUNICIPAL WASTE COMBUSTION RESEARCH PROGRAM

The municipal waste combustion (MWC) program is important because of the increasing concerns associated with land disposal of wastes and because of the potential for the emission of hazardous air pollutants including dioxins and furans when the waste is incinerated. The Laboratory is conducting engineering studies in support of the development of a NSPS for municipal waste combustors. AEERL is involved in three components of the MWC program: (a) field tests, (b) environmental engineering studies, and (c) program support.

One specific area of interest in the MWC program is the practice of co-firing municipal and other wastes in municipal waste combustors. Co-firing is defined as the combustion of waste or refuse-derived-fuel (RDF) in units originally designed to fire another fuel. For example, a sewage sludge incinerator or hog fuel boiler which uses RDF as an auxiliary fuel would be defined as a co-fired system. The program will include an assessment of municipal solid waste processing technology and types of RDF. The relationships between the physical and chemical properties of each type of RDF and the types of combustors in which it can be used will be addressed. Information will be developed on co-firing commercial operations, demonstrations, and trial burns. The waste, processing conditions, resulting RDF, combustion system, and flue gas cleaning equipment employed will be described to the extent needed to characterize the major design, operating, and performance features of each co-firing installation. Estimates will be made of the amount of RDF burned, and qualitative estimates will be made on effects of RDF firing on increased emission concentrations of particulate matter, carbon monoxide, sulfur dioxide, hydrochloric acid, polychlorinated dibenzo dioxins, and polychlorinated dibenzo furans.

Another area of interest to the Laboratory is the practice of simultaneous firing of two or more wastes, such as RDF and an auxiliary fuel. The current work will describe the types of MWC systems used for mixed waste/fuel firing and estimate the impact of mixed waste/fuel firing on combustor emissions. Model plants are to be defined and good combustion practices are to be postulated. The MWC program will also address the problems associated with burning hospital wastes in municipal waste combustors.

Data from current and new research activities and field tests will be collected and evaluated to support development of recommendations for good combustion practices (GCP). These collection and evaluation activities will include:

- Re-evaluation of process and emission data which are already contained in the existing OAQPS data base
- Evaluation of process and emission test data in the survey questionnaire responses obtained under the authority of Section 114 of the Clean Air Act

- Collection and evaluation of papers and reports on MWC combustion research

- Collection and evaluation of the data which result from new field tests which are not sponsored by EPA

AIR TOXICS CONTROL RAPID RESPONSE PROGRAM

A framework for rapid response to state and local agency needs relative to permitting and other support for air toxics control was initiated in FY 88, and this activity will be continued and expanded in FY 89. The framework incorporates existing laboratory research capabilities for carbon adsorption, laboratory facilities for the investigation of woodstove and other catalysts, and an air toxics control "Situation Room."

The carbon adsorption research laboratory will be used to experimentally investigate R&D needs identified by state and local environmental officials to the extent that resources and manpower permit. A plan has been developed for interaction with industry and EPA's air regulatory office concerning the application of research findings to the effective control of specific industrial VOC emission source categories in which relative humidity of the emission stream is a factor. Also, we are currently discussing with other EPA laboratories the feasibility of joint investigation of control approaches which may help reduce VOC emissions to the atmosphere. If such reductions can be achieved, the health and environmental problems associated with these emissions will also be reduced.

The rapid response framework also includes the air toxics control "Situation Room." The "Situation Room" will house available air toxics control models, including ESP models, carbon adsorption models, accidental release models, and general air toxics control models (the Control of Air Toxics or "CAT" model). The capability assembled in the "Situation Room" will allow rapid aid to state and local officials who need to assess the effectiveness of air toxics control approaches proposed in permit applications. The rapid response capability will also be enhanced by evaluation of other innovative air toxics control techniques. These include proof of concept for advanced control of hexavalent chromium and other toxic emissions from plating operations; laboratory characterization of MWC particles; and enhancement of the collection of asbestos and other fibrous materials by use of alternating electrical current.

CONCLUSION

The "easy fixes" for the control of volatile organic compounds have, for the most part, been expended. Standards have been developed and promulgated for the large point sources which emit more than 100 tons per year. We are left with a myriad of smaller sources which, when considered alone, contribute a small percentage of the total atmospheric loading. However, their combined

emissions make up a significant percentage of atmospheric loadings and contribute to the serious and worsening problems of ozone nonattainment, stratospheric ozone depletion, and adverse human health effects from direct exposure to hazardous air pollutants.

In the face of the unprecedented technical challenge presented by the complex mix of VOC's, HAP's, and CFC's, the Laboratory is developing and implementing a comprehensive engineering program aimed at providing the means for achieving environmental goals. The engineering research program is based on multiple approaches for VOC control, including prevention, product management, process management, and quality assurance for engineering controls. The program includes source identification, source assessment, conventional control technology assessment and improvement, and the development of innovative control techniques which may allow the control of small point and area sources which have not been controlled in the past. It is our hope that the program will produce the tools needed to deal effectively with the environmental problems associated with the emissions of VOC's, HAP's, and CFC's to the atmosphere.

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